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# PHOTOLYSIS MECHANISMS FOR POLLUTION ABATEMENT

Layton C. Kinney, et al

IIT Research Institute
Chicago, Illinois

October 1969

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27 Abstract

Photocatalytic oxidation of dissolved organic matter by irradiation of slurries of zinc titanate, zinc oxide, titanium dioxide, and beach sand was studied using sunlamps. The reaction appears to follow first order kinetics in most cases. Zinc oxide appears to be a superior catalyst for this purpose. Photocatalysts are widely distributed in nature, and photolytic oxidation is a mechanism whereby dissolved organic matter is oxidized in the natural environments of streams and lakes. Photolytic oxidation reduced the dissolved organic matter in a sample of domestic sewage by 50% and 75% during 24 hours and 70 hours, respectively. The limiting factor appears to be the activity of the photocatalyst. The most promising area of photolysis application will be in problems of industrial disposal where the concentrations of organic matter are high. (Carstea-USGS)

(WRSIC abstract) ←

| Abstractor | Institution |
|---|---|
| D. Carstea 3-24-70 | U. S. Geological Survey, Water Resources Div. |

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ROBERT A. TAFT WATER RESEARCH CENTER

REPORT NO. TWRC-13

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# PHOTOLYSIS MECHANISMS FOR POLLUTION ABATEMENT

## ADVANCED WASTE TREATMENT RESEARCH LABORATORY–XIII

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# PHOTOLYSIS MECHANISMS FOR POLLUTION ABATEMENT

by

Layton C. Kinney Victor R. Ivanuski

for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

This report is submitted in fulfillment of Contract No. 14-12-433 between the Federal Water Pollution Control Administration and the IIT Research Institute.

U. S. Department of the Interior
Federal Water Pollution Control Administration
Cincinnati, Ohio

October, 1969

# FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity, and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research studies carried out under the guidance of the technical staff of the FWPCA Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conslusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

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## ABSTRACT

Photocatalytic oxidation of dissolved organic matter by irradiation of slurries of zinc titanate ($Zn_2TiO_2$), zinc oxide (ZnO), titanium dioxide ($TiO_2$) and beach sand by sunlamps has been demonstrated. The reaction appears to follow first order kinetics in most cases. Zinc oxide appears to be superior for this purpose. At concentrations of 100 to 200 mg/l organic carbon, 80% of phenol, 67% benzoic acid, 44% acetic acid, 40% sodium stearate, and 16% sucrose were oxidized in 24 hrs with 10 gr/l zinc oxide catalyst. Continued illumination reduced organic carbon to a few mg/l in most cases.

The photocatalytic properties of illuminated beach sand (87% of phenol removed in 72 hr) strongly suggest that photocatalysts are widely distributed in nature and that photocatalytic oxidation is a mechanism whereby dissolved organic matter is oxidized in the natural environment in streams and lakes.

Dissolved organic matter in a sample of domestic sewage was reduced 50% in 24 hours and 75% in 70 hours. The limiting factor appears to be the activity of the photocatalyst since sunlamp intensity dropped approximately 80% without measurable decrease in oxidation rate. Improving catalyst activity by quenching from high temperature and/or by doping is proposed. The effects of ionizing radiation should be studied to determine the economic and technical advantages over UV. A recent publication[6] describing ZnO sensitized polymerization with both UV and gamma radiation reports that zinc oxide caused an enormous enhancement of the polymerizing effect of ionizing radiation in an aqueous system of calcium acrylate and acrylamide which suggests a corresponding increase in free radical generation.

At the present state of knowledge the most promising area of application appears to be in problems of industrial disposal where high concentrations of organic matter are involved since

the amount removed at constant irradiation intensity increases with increased concentration. Small residual concentrations might be economically removed by conventional means.

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# INTRODUCTION

This study was based on photocatalytic phenomena described in the literature and on experimentation conducted in IITRI laboratories. The interaction of photocatalysts with radiation below about 4200Å should produce active oxygen species which could destroy organic matter by complete oxidation to carbon dioxide and water.

Certain oxides, notably zinc oxide and titanium dioxide, are known to be photosensitizers or photocatalysts. Goodeve and Kitchener[1] obtained powerful photosensitization with $TiO_2$, studied by bleaching a blue dye under near-UV irradiation. Jacobsen[2] correlated outdoor chalking behavior of $TiO_2$ pigmented paints with the loss of reflectance of various $TiO_2$ pigmented media under sunlamp exposure. Weyl and Forland[3] proposed that atomic oxygen was dislodged by photons from rutile and other oxides; e.g., $SiO_2$ due to the asymmetric force field acting on the surface oxygen atoms.

Although photo-oxidation by zinc oxide has been much more extensively studied than $TiO_2$, no method to make it non-photoactive for outdoor pigment use has been found. The use of zinc oxide as a photoconductor in electrophotography has stimulated a great deal of study. Bauer and Neuweiler[4] were first to report the formation of hydrogen peroxide in near-UV-irradiated aqueous suspensions of zinc oxide. Markham et al.[5] studied zinc oxide photocatalysis extensively in aqueous systems and showed that sharply increased hydrogen peroxide concentrations were formed in aqueous media containing organic substances.

Yamamoto and Oster[6] reported that ZnO under UV excitation causes polymerization of vinyl monomers if water and oxygen are present. They concluded, on the basis of end group titration of polymethylmethacrylate polymers formed under these conditions, that hydroxyl radicals initiate the polymerization.

Work at IITRI showed that UV irradiated aqueous slurries of a specially prepared $TiO_2$, produce an oxidant similar to the

hydrogen peroxide formed in UV irradiated zinc oxide slurries. However, this oxidant does not give the amber pertitanic acid coloration specific for hydrogen peroxide. The formation of hydrogen peroxide in irradiated zinc oxide slurries has been confirmed by other investigators[5] by the titanic sulfate reaction. Both oxidants liberate, of course, iodine from potassium iodide. It was first thought the unknown oxidant was ozone; however, the absence of ozone odor at high concentrations and its appreciable solubility in water (concentrations of 500 ppm have been obtained) rule out this possibility.

Either oxidant (produced <u>in situ</u> by UV irradiation of ZnO and/or $TiO_2$) might provide a means of oxidizing dissolved organic matter in polluted water, since manufactured hydrogen peroxide and ozone have been used for this purpose.

## EXPERIMENTAL

### SCREENING OF PHOTOCATALYSTS

Because the level of oxidant obtainable in our previous work was low (8-10 mg/l), an investigation was undertaken to determine if greater concentrations of catalyst would produce higher levels of oxidant.

Initially, the light source was 4 G.E. 100W Fluorescent Daylight lamps on 4-inch centers in an aluminun foil lined reflector 18 inches from the sample. Samples of one-liter volume, in 180 by 100 mm crystallizing dishes, were stirred by magnetic stirrers separated from the dishes by Coolplates* which limited heating by the stirrer motors to about 2°C above ambient.

Catalysts initially examined included Photox 801, zinc oxide. (New Jersey Zinc Co.), titanium dioxide prepared by our own process, and a sample of zinc titanate. The latter had been found to be destructive to organic vehicles under UV light.

Initial experiments conducted at 25 ppm verified previous data and indicated that zinc titanate was a photocatalyst on the basis of an initial equilibrium oxidant level of approximately 5 mg/l as $H_2O_2$.

In an effort to raise oxidant concentrations, catalyst loadings were increased from 1-5%; however, this had the opposite effect in that equilibrium concentrations dropped substantially.

We concluded that the catalyst was decomposing the oxidants and that once the shaded fraction exceeded the irradiated oxide, the equilibrium concentration dropped.

This effect was quite unexpected, since Markham and Laidler[5], working with fairly concentrated slurries (0.1 g ZnO/25 ml $H_2O$) had obtained high concentrations (170 mg/l) of $H_2O_2$. Their results are attributable to the fact that the various organic substances they worked with inhibited the decomposition reaction,

---

*Thermodyne Corporation Dubuque, Iowa.

thus strongly favoring oxidant formation.

Since the dilute slurries absorb only a small fraction of the radiation, use of an oxidized metal surface as the photocatalyst was investigated. In this way access of the solution to shaded surfaces would be decreased or prevented. Also, in many cases, it was thought the oxidized surface would be a more efficient absorber of radiation than the white pigments. On this assumption a number of metals were examined including zinc, copper, nickel, bronze, titanium, and tin.

In some cases the metal was heavily oxidized by heating and in others it was used with the normal invisible oxide of the metal. Many of these materials, especially zinc and copper, looked quite promising at first, on the basis of oxidant levels which in the case of zinc rose rapidly at first to about 25 mg/l $H_2O_2$; however, as the formation of zinc oxide proceeded it dropped to 2.5 mg/l in about 3 days.

In addition to oxidized metals it was found that a number of other substances show photocatalytic properties, for example, Ottawa silica sand and two man-made pigments which were largely $Fe_2O_3$ and $Fe_3O_4$. Two dimensional catalyst surfaces such as ceramic porcelain ware and Pyrex as well as films of zinc undecylate developed oxidant concentrations of 5-10 mg/l when illuminated for a week or so. Of the oxidants formed, all were of the non-hydrogen peroxide variety (with the exceptions of irradiated zinc and tin metal plates) as determined by their negative pertitanic acid tests with titanic sulfate reagent. Since we have not yet identified oxidant "x", as we call it, and since it is detected by the oxidation of potassium iodide these oxidants were both reported as hydrogen peroxide as determined by a spectrophotometric starch iodide method described in detail in the Appendix.

We concluded that there must be many substances, other than man-made, which exhibit photocatalytic properties; in all probability ordinary beach sand contains photocatalytic minerals. To test this hypothesis, sand was obtained from a nearby beach

and exposed to daylight fluorescent radiation.

After 2 days of exposure, of a thin layer of sand, the oxidant level rose to 3.5 mg/l. A thick layer of sand produced a faint but definite trace of oxidant which remained constant after a few days of exposure. The difference is attributed to the enhancement of the reverse reaction in the thick layer. Apparently, our hypothesis was correct. Oxidant "x" is being formed and decomposed on shores and beds of streams where natural photocatalysts are illuminated by solar energy. We theorized that photocatalysis is a mechanism of nature to remove organic pollutants in addition to non-catalytic photolysis, autoxidation and biodegradation. This theory was subsequently verified by brief, but conclusive, experiments demonstrating the removal of organic contaminants from water by simulated sunlight. These experiments are described in the following section.

The site from which sand samples were obtained was substantially that from which Pettijohn[7] obtained his. Since this is natural beach, it is assumed the mineral content is similar to that he reports. The principal minerals found by Pettijohn were garnet (Mg, Ca, or Fe-Al silicate); augite ($CaO \cdot MgO \cdot 2SiO_2$); Hornblende ($3[MgFe]O \cdot CaO$); $SiO_2$; ilmenite (FeO 48%, $TiO_2$ 52%), and magnetite ($Fe_3O_4$) along with calcium and magnesium carbonaceous minerals.

## PHOTOXIDATION OF ORGANIC SUBSTANCES

Although we had hoped to find a catalyst superior to the powdered oxides initially investigated, it became increasingly evident that oxidant level, per se, was not a valid indication of organic oxidation effectiveness. Consequently, efforts were directed toward actual oxidation studies which were monitored by the Beckman Total Organic Carbon Analyzer.

The first experiments, run in zinc pans, were inconclusive. Although linear alkylate sulfonate (LAS) was oxidized, we suspected that galvanic factors due to the formation of oxygen concentration cells were involved since oxidation in dark samples

approached that of illuminated samples. For this reason further work with oxidized metal surfaces was abandoned.

The first definite photo-oxidation of an organic substance obtained is shown in Figure 1. The apparent initial rise in organic carbon is not understood; it may have been due to desorption of an organic substance from the catalyst (20 g zinc titanate in 350 ml $H_2O$). The superiority of the sunlamps* whose emission is almost entirely in the 3000-4000Å region over the G.E. Daylight fluorescent lamps, is clearly evident from the Figure. This superiority was somewhat surprising since oxidant levels were about the same under each source. This demonstrates that oxidant level alone is not a valid indication of organic oxidation rate. With few exceptions, subsequent tests were run under sunlamps. These samples were exposed in 180 mm-diameter Pyrex dishes, 75 mm deep without agitation. In view of its poor showing in these tests, further work with $ZnTiO_4$ was discontinued.

Figure 2 demonstrates oxidation of both phenol and benzoic acid and the $H_2O_2$ concentration does increase in the presence of organic matter as reported by Markham and Laidler[5]. The higher values obtained by those authors are probably due to the fact they used pure oxygen. Markham and Laidler, as well as Oster and Yamamoto[8], showed oxygen to be essential to the photo-oxidation by zinc oxide.

The samples in Figure 2 were exposed in 180 x 100 mm crystallizing dishes and stirred magnetically. Dishes were placed eccentrically which helps to prevent the catalyst from settling. Analyses for total organic carbon (TOC) and oxidant were made on "whole samples", i.e., catalyst and solution which avoids artifacts due to adsorption of degradation products on the catalyst which appears to vary in the course of the test. In hundreds of tests, the small quantity of oxide introduced into the combustion zone of the organic carbon analyzer had no apparent effect.

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*8 twenty watt sunlamps on 4" centers with an aluminum reflector 18" from the sample.

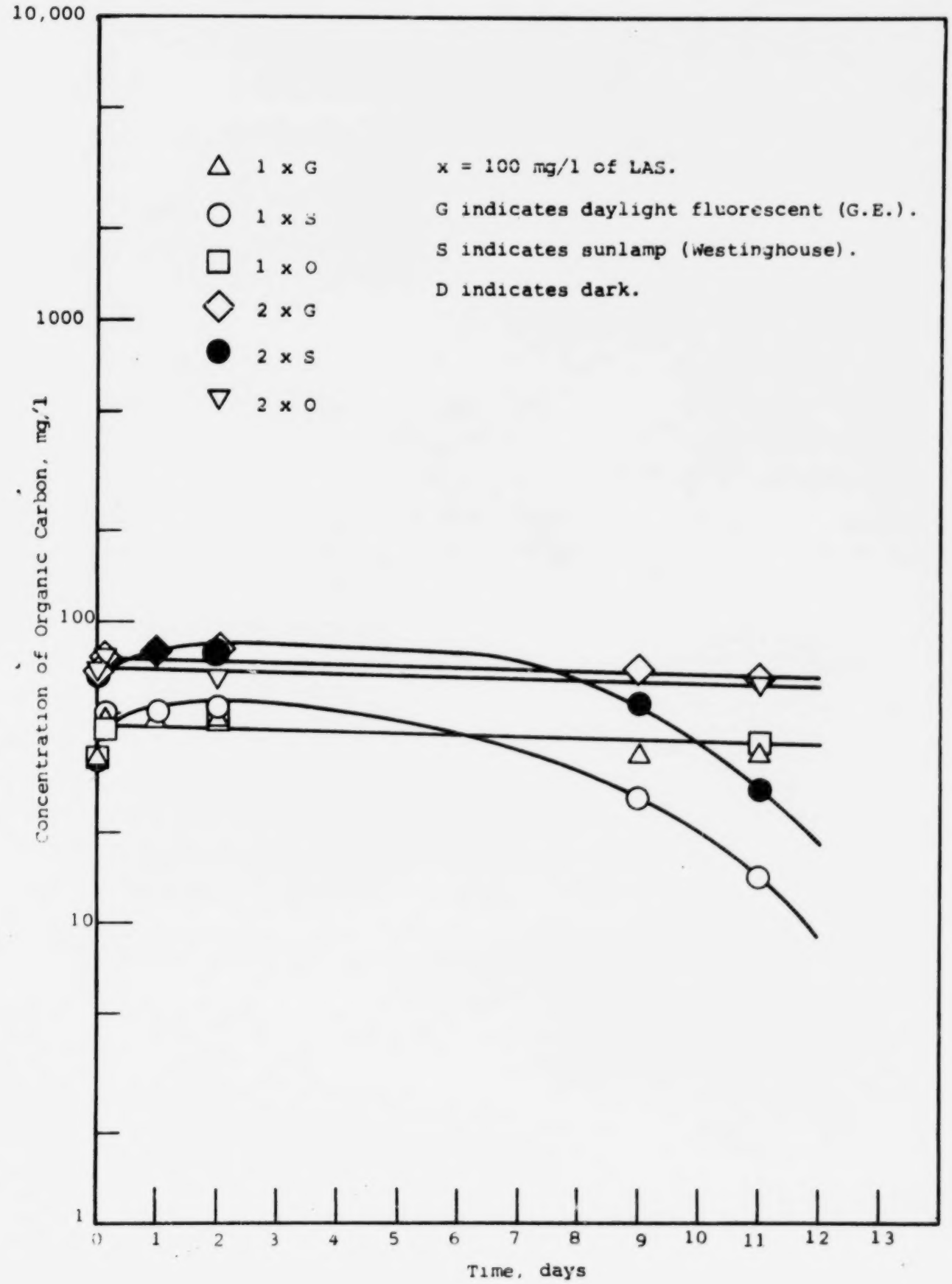


Figure 1

EFFECT OF LIGHT SOURCE ON LAS REMOVAL
BY ZINC TITANATE

Table 1

EFFECT OF LIGHT SOURCE ON LAS REMOVAL BY ZINC TITANATE

| | Concentration of Organic Carbon, mg/l | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Time, day | | | | | | | | | |
| | 0 | | 3[a] | | 1 | | 2 | | 9 | | 11 | |
| Sample | Carbon | pH | Carbon | pH | Carbon | pH | Carbon | pH | Carbon | pH | Carbon | pH |
| 1xG | 35.0 | 7.2 | 47.5 | 6.1 | 47.5 | | 48.5 | | 36.0 | 5.9 | 36.0 | 6.0 |
| 1xS | 35.0 | 7.2 | 48.5 | 6.3 | 50.0 | | 51.0 | | 26.0 | 6.1 | 14.5 | 6.0 |
| 1xD | 35.0 | 7.2 | 45.0 | 6.4 | | | 50.0 | | | | 39.0 | 5.8 |
| 2xG | 69.5 | 7.0 | 76.0 | 6.2 | 81.0 | | 80.0 | | 69.5 | 4.8 | 65.0 | 5.4 |
| 2xS | 69.5 | 7.0 | 74.0 | 6.2 | 80.5 | | 81.0 | | 53.5 | 4.7 | 28.0 | 5.8 |
| 2xD | 69.5 | 7.0 | 74.0 | 6.4 | | | 66.0 | | | | 62.0 | 5.8 |

[a]Hours.

x = 100 mg/l of LAS.

G indicates daylight fluorescent (G.E.).

S indicates sunlamp (Westinghouse).

D indicates dark.

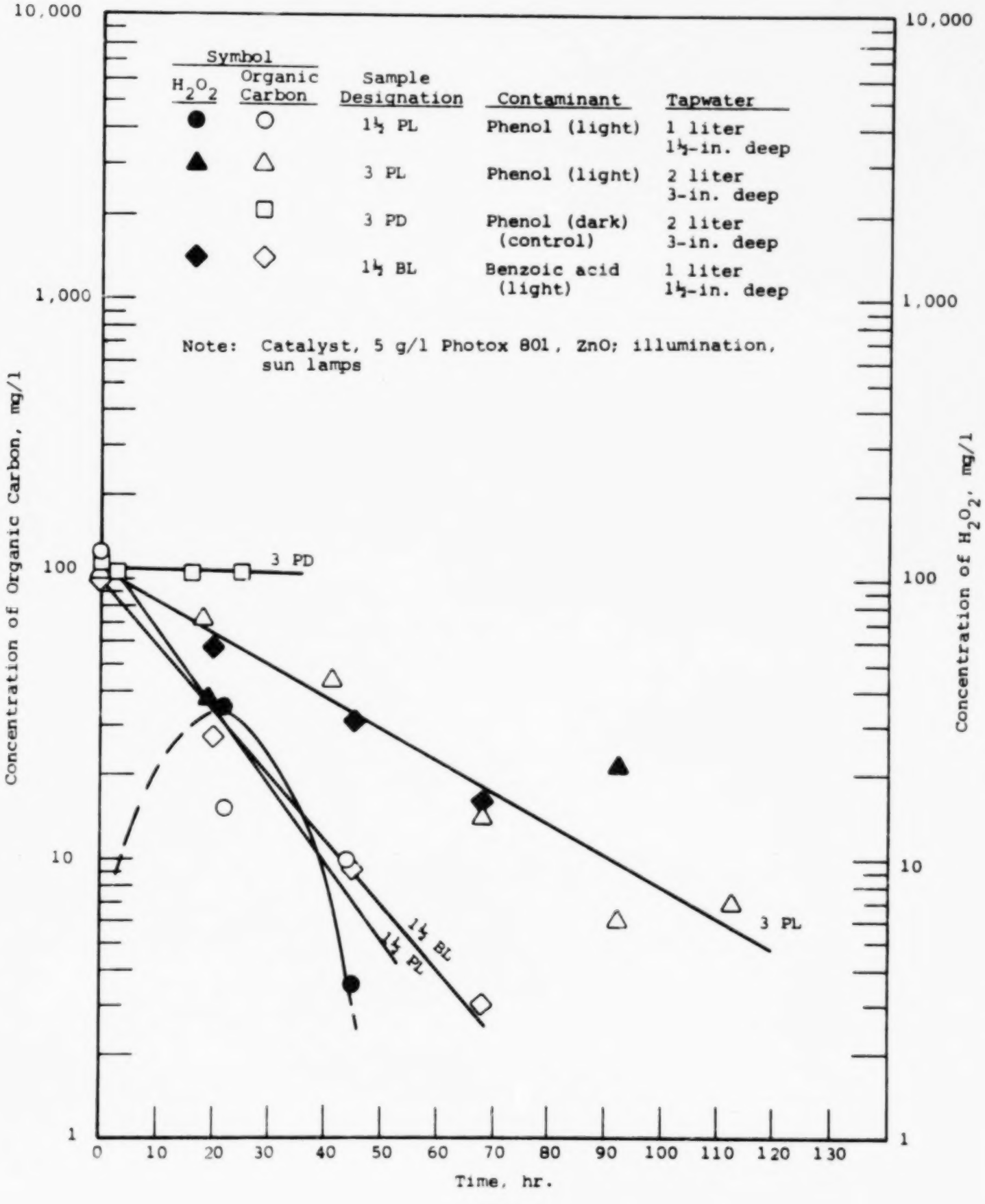


Figure 2

EFFECT OF DEPTH OF SAMPLE ON OXIDATION OF PHENOL AND COMPARISON OF PHENOL AND BENZOIC ACID OXIDATIONS

Table 2

EFFECT OF DEPTH OF SAMPLE ON OXIDATION OF PHENOL AND COMPARISON OF PHENOL AND BENZOIC ACID OXIDATIONS (Catalyst, 5 g/l, Photox 801 (N.J.Z.)

| | Concentration of Organic Carbon and $H_2O_2$, mg/l | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Sample | | | | | | | |
| | 1-1/2[a] PL | | 3 PL | | 3 PD[b] | | 1-1/2 BL | |
| Time, hr | Organic Carbon | $H_2O_2$ | Organic Carbon | $H_2O_2$ | Organic Carbon | $H_2O_2$ | Organic Carbon | $H_2O_2$ |
| 0 | 122 | | 104 | | 114 | | 101 | |
| 3 | | | | | 106 | | | |
| 18 | | | | | 106 | | | |
| 19 | | | 73 | 38 | | | | |
| 20 | | | | | | | 27 | 56 |
| 22 | 15 | 35 | | | | | | |
| 25 | | | | | 104 | | | |
| 41 | | | 44 | | | | | |
| 44 | 11 | 3.5 | | | | | | |
| 45 | | | | | | | 9 | 32 |
| 68 | | | 14 | | | | 3 | 16 |
| 92 | | | 6 | 23 | | | | |
| 112 | | | 7 | 8 | | | | |

[a] 1-1/2-in. depth, 3-in. depth, etc.

[b] Control sample kept in dark.

Note: The phenol sample concentrations were approximately 0.15 g/l, and the benzoic acid sample concentration was also approximately 0.15 g/l.

| Sample Designation | Contaminant | Tapwater |
|---|---|---|
| 1½ PL | Phenol (light) | 1 liter 1½-in. deep |
| 3 PL | Phenol (light) | 2 liter 3-in. deep |
| 3 PD | Phenol (dark) (control) | 2 liter 3-in. deep |
| 1½ bL | Benzoic acid (light) | 1 liter 1½-in. deep |

First order kinetics were observed for the oxidation of both phenol and benzoic acid. The decrease in hydrogen peroxide concentration after a sharp initial rise appears to follow a similar path, though the data are incomplete. Control samples stored in the dark showed no reaction between either photocatalytically produced oxidant or $H_2O_2$ with organic matter. This suggests that the oxidation is directly associated with the active oxygen species released by the radiation.

Figure 3 represents an effort to assess the importance of catalyst loading on phenol oxidation. Samples were magnetically stirred in 100 mm by 180 mm crystallizing dishes. The data indicate only slight gains by increased catalyst loading from 2.5 g/l - 10 g/l, whereas at 0.5 and 0.1 g/l proportionately lower oxidation rates were encountered. This suggests that once all the incident light is absorbed, additional catalyst gives only slightly improved removal of organic carbon.

Despite the apparent lack of effect of excess catalyst, a recirculation system was devised to keep all the catalyst in suspension.

Several three gallon Pyrex bottles were cut off 2 inches from the mold line at the shoulder and the bottom was discarded. The neck was reduced in diameter and a 29/42 standard taper female fitting was fused to the reduced neck. A male taper fitting with a suitable opening for drainage was attached by springs and the assembly was inverted on an iron tripod. The bottom drain was connected to a the suction side to a peristaltic pump with a Viton tube after first passing the slurry through a water-cooled condenser. The discharge of the pump was connected to a 10 mm tube with a right angle bend terminating in a 3 mm nozzle which was arranged at the outer periphery of the vessel so that the discharge imparted a circular motion to the contained slurry. In this manner the mixture was constantly recirculated at a rate of about 1 l/min. Additional aeration was provided by a sintered glass gas dispersion tube immersed to within about 1 inch from the pump intake. Air from an aquarium

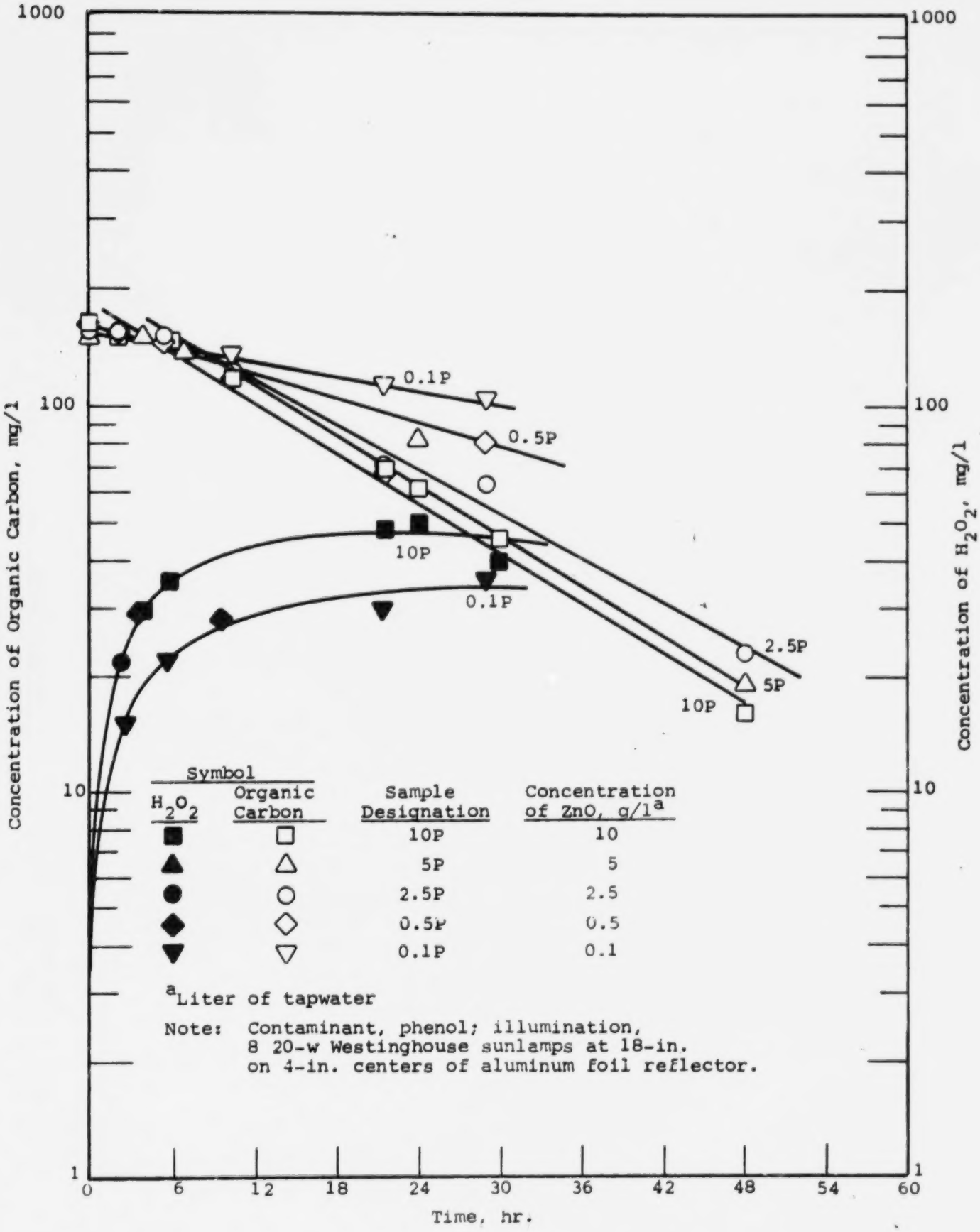


Figure 3

EFFECT OF VARIOUS ZnO LEVELS
ON MAGNETICALLY STIRRED SAMPLES

Table 3

EFFECT OF VARIOUS ZINC OXIDE LEVELS ON MAGNETICALLY STIRRED SAMPLES

| Sample | Time, hr | Concentration, mg/l | | Time, hr | Concentration, mg/l | | Time, hr | Concentration, mg/l | | Time, hr | Concentration, mg/l | | Time, hr | Concentration, mg/l | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Organic Carbon | $H_2O_2$ | | Organic Carbon | $H_2O_2$ | | Organic Carbon | $H_2O_2$ | | Organic Carbon | $H_2O_2$ | | Organic Carbon | $H_2O_2$ |
| 10P | 0 | 161 | | 2.3 | 152 | | 4 | | 29.6 | 5.8 | 144 | 35 | 10.7 | 118 | |
| 5P | 0 | 150 | | 4 | 150 | | | | | 7 | 137 | | | | |
| 2.5P | 0 | 155 | | 2.2 | 162 | 22 | | | | 5.4 | 151 | | 10.7 | 125 | |
| 0.5P | 0 | 161 | | 2.2 | 154 | | 3.5 | | 28.5 | 5.6 | 149 | | 10.7 | 118 | 28 |
| 0.1P | 0 | 155 | | 2.2 | 152 | 15 | | | | 5.8 | 153 | 22 | 10.5 | 134 | |
| (cont.) | | | | | | | | | | | | | | | |
| 10P | 21.7 | 68 | 48 | 24 | 61<br>51[a] | 50 | 30 | 45 | 38 | 48 | 16<br>6[a] | | | | |
| 5P | 24 | 83 | | | | | | | | 48 | 19 | | | | |
| 2.5P | 21.5 | 71 | | 29 | 63 | | | | | 48 | 23 | | | | |
| 0.5P | 21.5 | 72 | | 29 | 82 | | | | | | | | | | |
| 0.1P | 21.7 | 111 | 30 | 29 | 103 | 36 | | | | | | | | | |

[a]Centrifuged.

| Sample Designation | Concentration of ZnO, g/l[a] |
|---|---|
| 10P | 10 |
| 5P | 5 |
| 2.5P | 2.5 |
| 0.5P | 0.5 |
| 0.1P | 0.1 |

pump was provided at a rate of 60 ml/min.

Figure 4 depicts results of recirculation at various catalyst loadings and shows a sharp increase at 10 g/l. At catalyst loadings of 2 and 5 g/l, however, there seems little effect. Even with the recirulcation system sedimentation of the catalyst occurred in certain instances. It is interesting to note the behavior of the $H_2O_2$ concentration in these tests. With phenol contaminant the level drops more rapidly with higher catalyst loading and shows a general relationship to the residual contaminant. This does not hold true for acetic acid however, since the concentration drops sharply while the residual contaminant is still high. The $H_2O_2$ concentration for sucrose (Figure 7) appears to level off and remain high despite the high catalyst loading. A better understanding of these phenomena might provide useful insights into the effects of pollutants in the natural environment.

Figure 5 shows little difference between magnetic stirring or recirculation if one takes into account the lower starting concentration of samples 5P, 1½Bl, and 1½Pl. The curve for the 1½Pl sample may be the result of sampling errors.

Figure 6, on the other hand, shows a clearcut advantage of recirculation over magnetic stirring. Figure 7 shows a comparison of phenol with sucrose, sodium stearate and two examples of acetic acid oxidation. The difference in the two acetic acid runs is due to the sequence of adding the zinc oxide and acetic acid. The acetic acid curve on Figure 4 was obtained by first adding the acid to tap water and then adding the zinc oxide. This method removes all of the inorganic carbon. However, over the course of the oxidation inorganic carbon returned to the original value. In a later experiment, shown in Figure 7, the zinc oxide was added before the acetic acid, which results in the formation of zinc acetate which is more slowly oxidized, accompanied by a substantial rise in inorganic carbon means that one product of oxidation of zinc acetate is zinc carbonate. From Figure 7, it can be seen that phenol, acetic acid (added

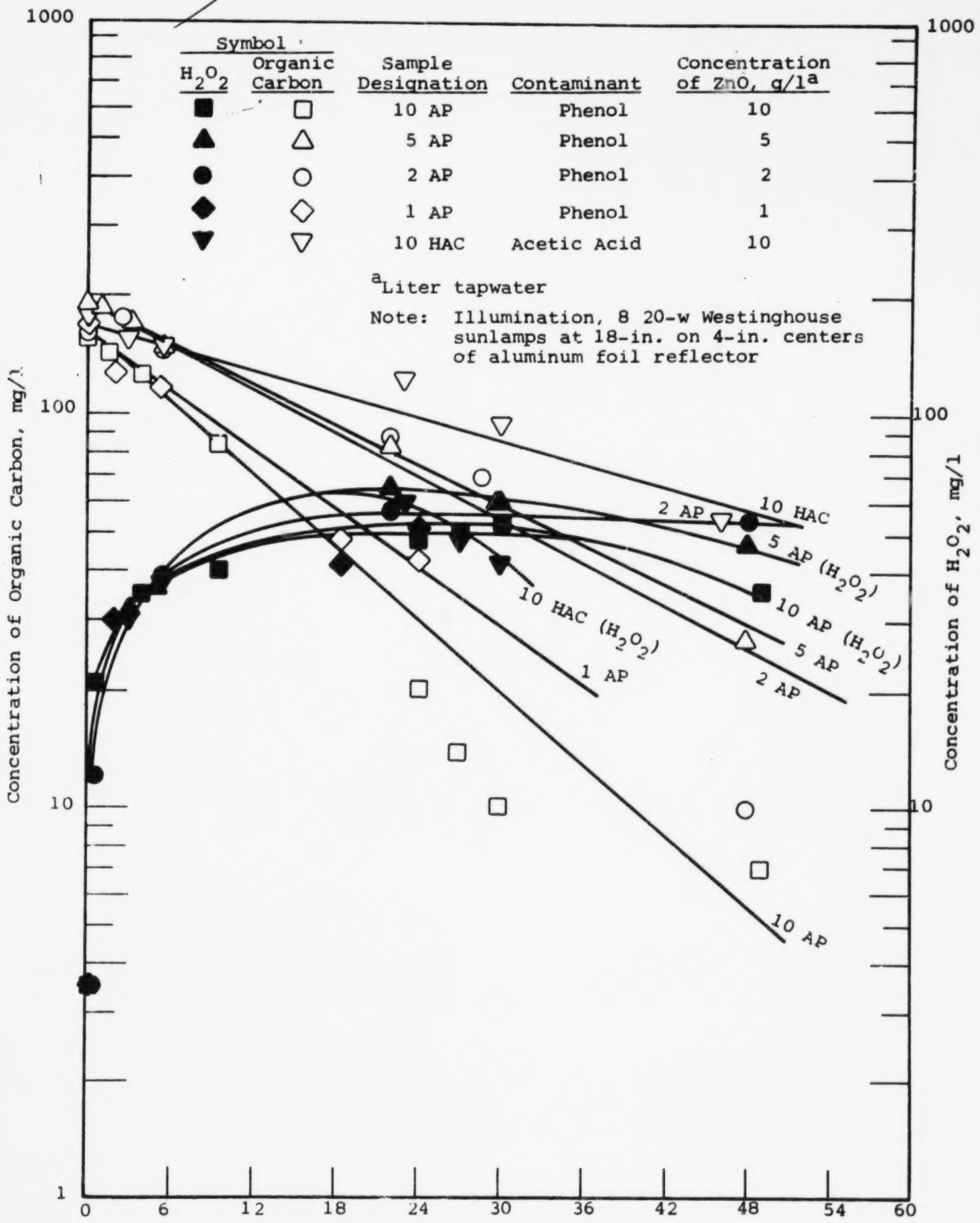


Figure 4

EFFECT OF ZINC OXIDE LOADING
ON RECIRCULATED SAMPLES

Table 4

EFFECT OF ZINC OXIDE LOADING ON RECIRCULATED SAMPLES

| Sample | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 AP | 0 | 157.5 | 3.5 | .75 | | 21 | 1.5 | 141 | | 4 | 126 | 35 | 9.5 | 82 | 40 |
| 5 AP | 0 | 190 | | 1 | 183 | | 3.1 | 170 | 31 | 5.3 | 146 | 37 | 22 | 82 | 66 |
| 2 AP | 0 | 160 | 3.5 | .3 | | 12 | 2.4 | 175 | | 5.2 | 147 | 38 | 22 | 88 | 57 |
| 1 AP | 0 | 170 | 3.5 | 2 | 139 | 30 | 5.3 | 115 | 39 | 18.7 | 48 | 42 | 24 | 43 | 52[a] |
| 10 HAC | 0 | 178 | | 3 | 156 | 30 | 5.5 | 148 | 37 | | | | 23 | 124 | 60 |
| (cont.) | | | | | | | | | | | | | | | |
| 10 AP | 24 | 20 | 48 | 27 | 14 | 50 | 30 | 10 | 53 | 49 | 7 | 36 | | | |
| 5 AP | 29.7 | 60 | 60 | 48 | 27 | 47 | | | | | | | | | |
| 2 AP | 28.8 | 70 | 60 | 48 | 10 | 54 | | | | | | | | | |
| 10 HAC | 30 | 95 | 42 | 46 | 55 | 50 | | | | | | | | | |

[a]Discontinued.

| Sample Designation | Contaminant | Concentration of ZnO, g/l[a] |
|---|---|---|
| 10 AP | Phenol | 10 |
| 5 AP | Phenol | 5 |
| 2 AP | Phenol | 2 |
| 1 AP | Phenol | 1 |
| 10 HAC | Acetic Acid | 10 |

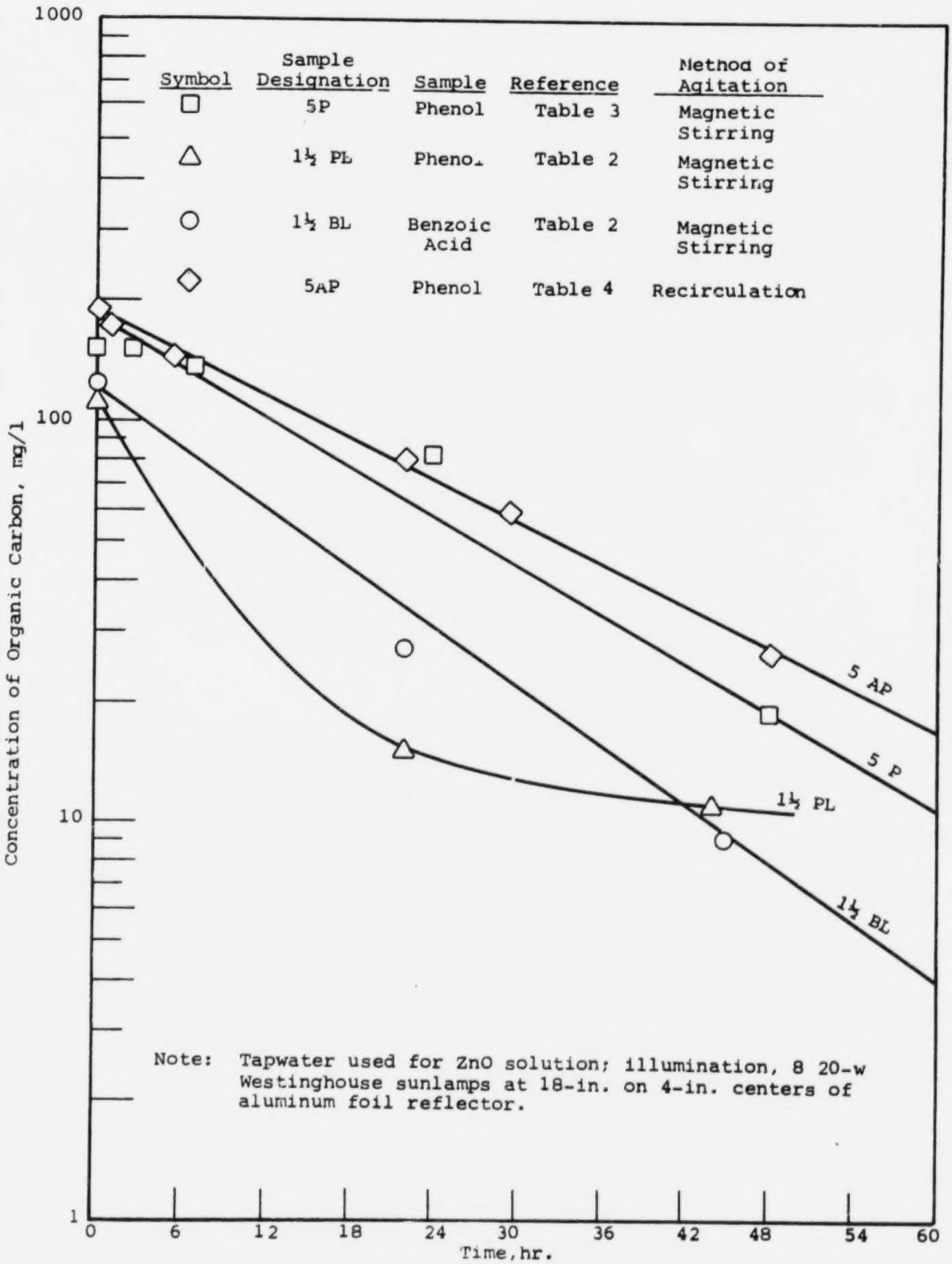


Figure 5

COMPARISON OF AGITATION METHODS
USING A ZnO CONCENTRATION OF 5 g/l

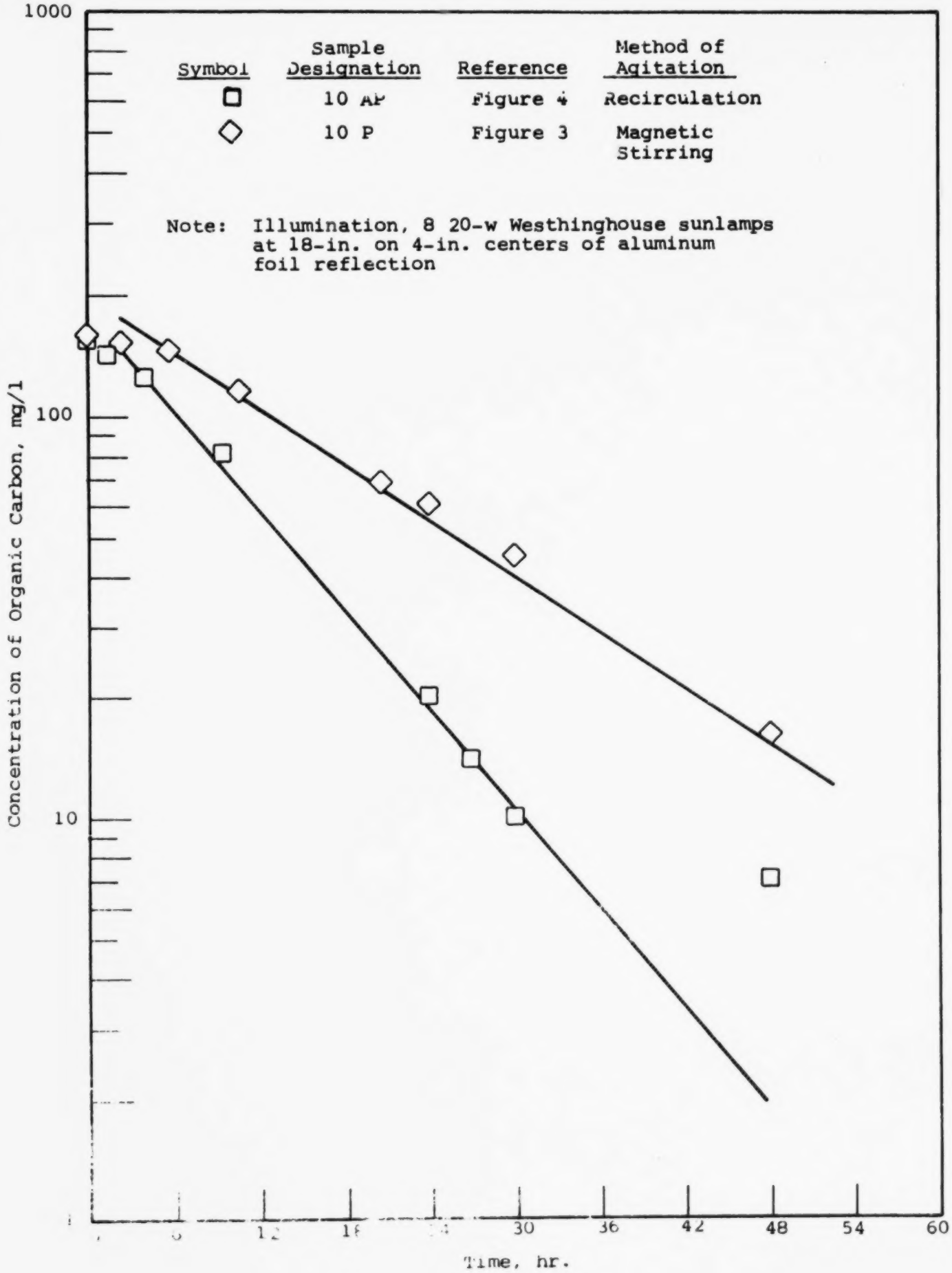


Figure 6

COMPARISON OF AGITATION METHODS ON OXIDATION OF PHENOL USING 10 g OF ZINC OXIDE

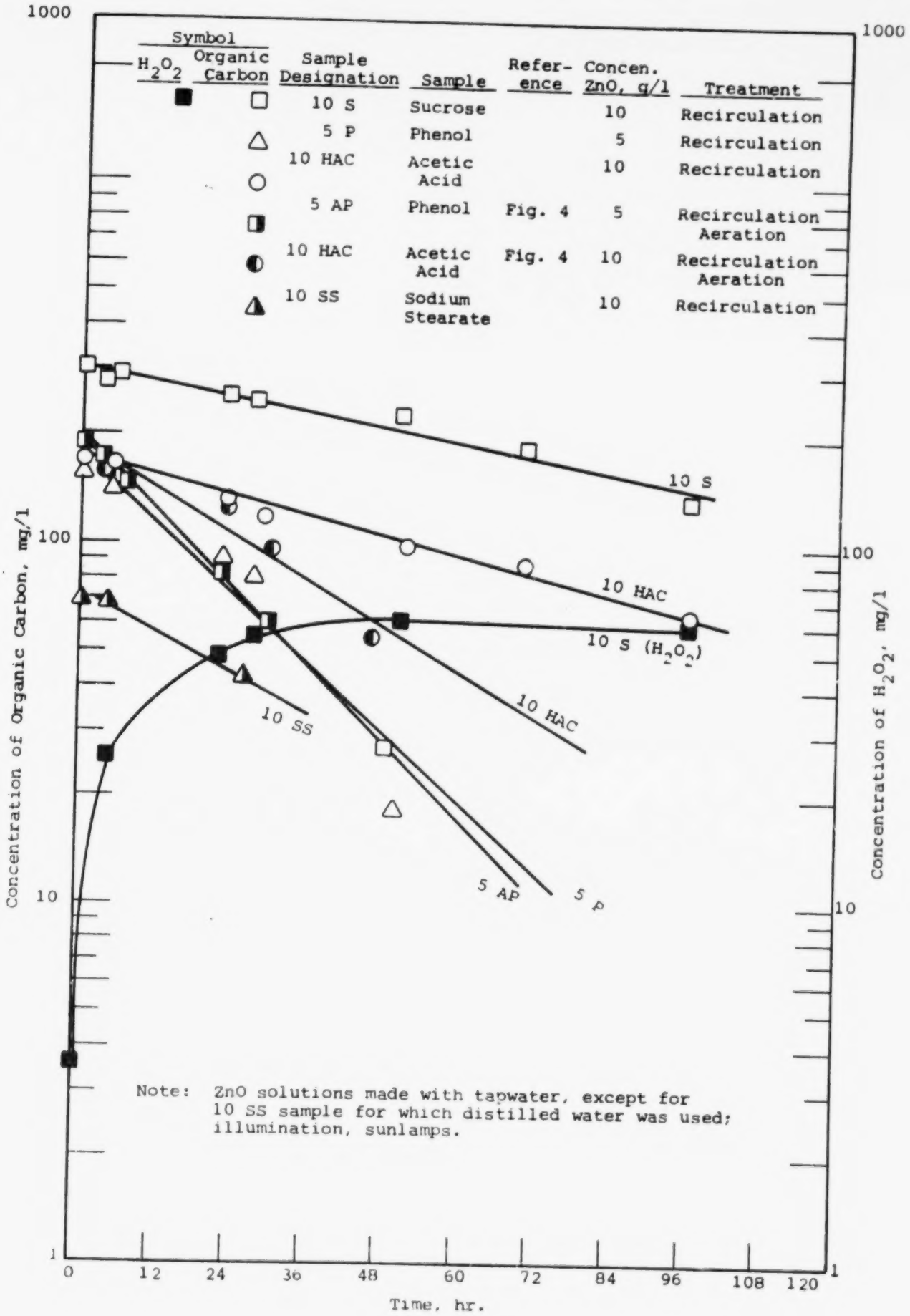


Figure 7

COMPARISON OF AERATED WITH NONAERATED RECIRCULATED SLURRIES, ALSO OXIDATION OF ACETIC ACID, SUCROSE, PHENOL, AND SODIUM STEARATE

Table 5
(Data plotted in Figure 7)

COMPARISON OF AERATED WITH NONAERATED RECIRCULATED SLURRIES,
ALSO OXIDATION OF ACETIC ACID SUCROSE, PHENOL, AND SODIUM STEARATE

| Sample | Contaminant | Concentration of ZnO, g/l | Time, hr | Concentration mg/l | | Time, hr | Concentration mg/l | | Time, hr | Concentration mg/l | | Time, hr | Concentration mg/l | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Organic Carbon | $H_2O_2$ | | Organic Carbon | $H_2O_2$ | | Organic Carbon | $H_2O_2$ | | Organic Carbon | $H_2O_2$ |
| 10S[a] | Sucrose | 10 | 0 | 296 | | 3.5 | 276 | 25 | 5.3 | 289 | | 22.9 | 252 | 48 |
| 5P[a] | Phenol | 5 | 0 | 152 | | 4.3 | 139 | -- | -- | -- | | 22.3 | 92 | |
| 10HAC[a] | Acetic Acid | 10 | 0 | 166 | | 5.0 | 166 | -- | -- | -- | | 22.7 | 130 | |
| 10SS[a] | Sodium Stearate | 10 | 0 | 69 | | 4.1 | 67 | 8 | 25 | 42 | | discontinued | | |
| (cont.) | | | | | | | | | | | | | | |
| 10S | | | 27.7 | 249 | 55 | 50 | 228 | 62 | 70 | 188 | | 46 | 133 | 60 |
| 5P | | | 27.3 | 80 | -- | 50 | 18 | | 70 | discontinued | | | | |
| 10HAC | | | 28.5 | 118 | -- | 51 | 97 | | 70 | 89 | | 96 | 64 | -- |

[a]Samples recirculated without aeration.

| Sample Designation | Sample | Reference | Concen. ZnO, g/l | Treatment |
|---|---|---|---|---|
| 10 S | Sucrose | | 10 | Recirculation |
| 5 P | Phenol | | 5 | Recirculation |
| 10 HAC | Acetic Acid | | 10 | Recirculation |

| Sample Designation | Sample | Reference | Concen. ZnO, g/l | Treatment |
|---|---|---|---|---|
| 5 AP | Phenol | Fig. 4 | 5 | Recirculation Aeration |
| 10 HAC | Acetic Acid | Fig. 4 | 10 | Recirculation Aeration |
| 10 SS | Sodium Stearate | | 10 | Recirculation |

before zinc oxide), sodium stearate and sucrose are oxidized with increasing difficulty in that order. The sodium stearate curve represents zinc stearate oxidation. Figure 7 also compares recirculated aerated samples with non-aerated recirculated samples.

These results demonstrate that aeration does not enhance the oxidation mechanism. No differences in dissolved oxygen were noted, being in both cases, saturated at the temperature of the tests.

To obtain a more coherent picture of the effects of agitation as well as to assess the degree to which air stripping and/or autoxidation are involved, the experiments illustrated in Figure 8 were conducted.

This figure shows a comparison of various methods of agitation with respect to phenol removal. Comparison of the aerated samples in the dark and the illuminated samples, without catalyst in each case, shows that part of the phenol removal is by stripping and/or autoxidation. The additional removal under illumination (without ZnO catalyst) are photocatalytic oxidation by Pyrex which is a weak photocatalyst*. A similar acceleration occurs with magnetically stirred samples in the light without catalyst compared to similar samples in the dark. Phenol added to distilled water stirred in polyethylene (not shown) had a slope closely paralleling the magnetically stirred sample in the dark.

Since much of the increase in oxidation rate was due to air stripping in both the recirculated and the aerated samples, we decided to return to magnetic stirring because this method shows the greatest effect due to the presence of catalyst. However, none of the methods keeps the catalyst entirely in suspension. Initially we thought as long as sufficient catalyst was in suspension to absorb all the incident radiation, an excess would do no harm. This is true if the pigment all remains in suspension;

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*Distilled water magnetically stirred reaches an equilibrium concentration of oxidant "x" as $H_2O_2$ of 4 mg/l when illuminated by G.E. Daylight fluorescent lamps for 6 days.

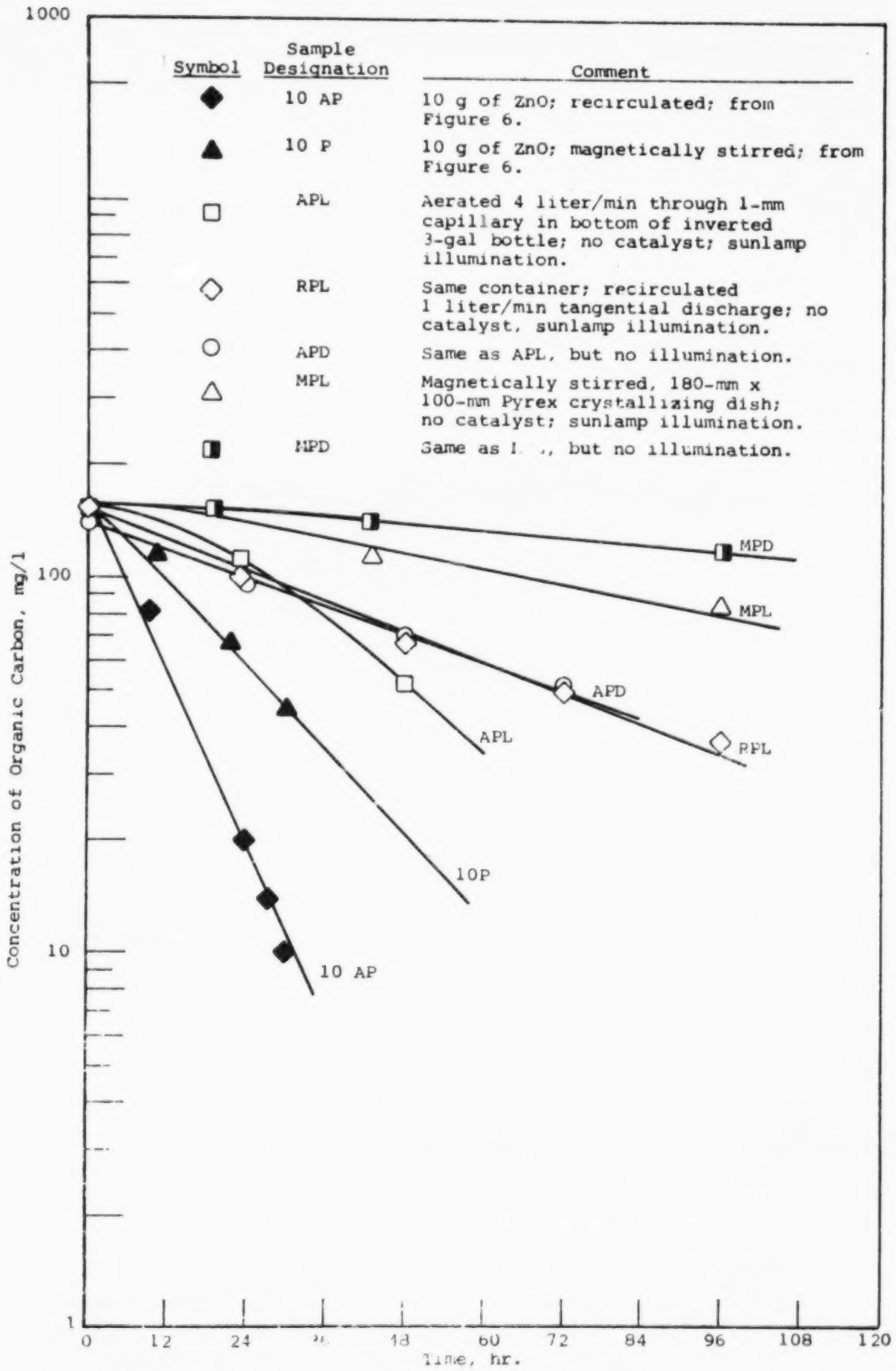


Figure 8

COMPARISON OF VARIOUS AGITATION METHODS IN REMOVING PHENOL

Table 6
(Plotted in Figure 8)

COMPARISON OF METHODS OF AGITATION ON OXIDATION OF PHENOL USING 10g OF ZINC OXIDE

| Sample | Time, hr | Concentration mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration mg/l Organic Carbon | $H_2O_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| APL | 0 | 154 | | 23 | 112 | -- | 48 | 52 | -- | 72 | -- | |
| RPL | 0 | 153 | | 23 | 101 | -- | 48 | 67 | 3.0 | 72 | 50 | |
| APD | 0 | 140 | | 24 | 97 | -- | 48 | 70 | -- | 72 | 51 | |
| MPL | 0 | 155 | | 19 | 152 | 1.5 | 43 | 115 | -- | 96 | 85 | |
| MPD | 0 | 157 | | 19 | 155 | -- | 43 | 140 | -- | 96 | 112 | |

| Sample Designation | Comment | Sample Designation | Comment |
|---|---|---|---|
| APL | Aerated 4 liter/min through 1-mm capillary in bottom of inverted 3-gal bottle; no catalyst; sunlamp illumination. | APD | Same as APL, but no illumination. |
| RPL | Same container; recirculated 1 liter/min tangential discharge; no catalyst, sunlamp illumination. | MPL | Magnetically stirred, 180-mm x 100-mm Pyrex crystallizing dish; no catalyst; sunlamp illumination. |
| | | MPD | Same as MPL, but no illumination. |

however, if the contaminant is appreciably adsorbed on settled catalyst, it is protected from oxidation and may only become available for oxidation through diffusion, thereby slowing the process.

## PHOTOCATALYTIC OXIDATION OF PHENOL WITH $TiO_2$ AND BEACH SAND

Since we had on hand only limited amounts of the special $TiO_2$ catalyst prepared in our previous work, it was necessary to prepare it. The $TiO_2$ was obtained from New Jersey Zinc Co. in slurry form and did not contain the stabilizing additives, e.g., silicates that are normally added to minimize photocatalysis in commercial pigments. This slurry was washed chloride-free and nearly sulfate-free. The resultant cake was dried at 100°C. Figure 9 compares oxidation of phenol by various types of $TiO_2$. Based on limited tests the optimum calcination temperature is about 850°C since at 48 and 72 hrs, the 850°C sample is better than either the 825°C or 875°C sample. The apparent increase in rate of oxidation with time is interesting. In subsequent tests (not shown), a commercial anatase and an active $TiO_2$ prepared some years ago by the IITRI technique were also compared under the same conditions; both were definitely inferior to the samples shown in Figure 9 in oxidation of phenol under the same conditions.

A brief experiment was conducted to determine the effectiveness of beach sand. These data are shown graphically in Figure 10 and support our previously stated conviction that photo-oxidation by natural catalysts under solar irradiation is a mechanism of nature for the removal of organic matter from streams and lakes. In these tests, 300 g of water washed beach sand were placed in the recirculation container described previously and 4 l/min of room air was pumped through from the bottom. This produced much less agitation in sand than anticipated and much less than sample APD, since the column of water being agitated was about six times longer due to the absence of sand. The true comparison is between 300 PBD and 300 PBL. The leveling off of 300 PBL at 22 mg/l is believed due to the presence of a refractory organic substance leaching out of the sand or possibly

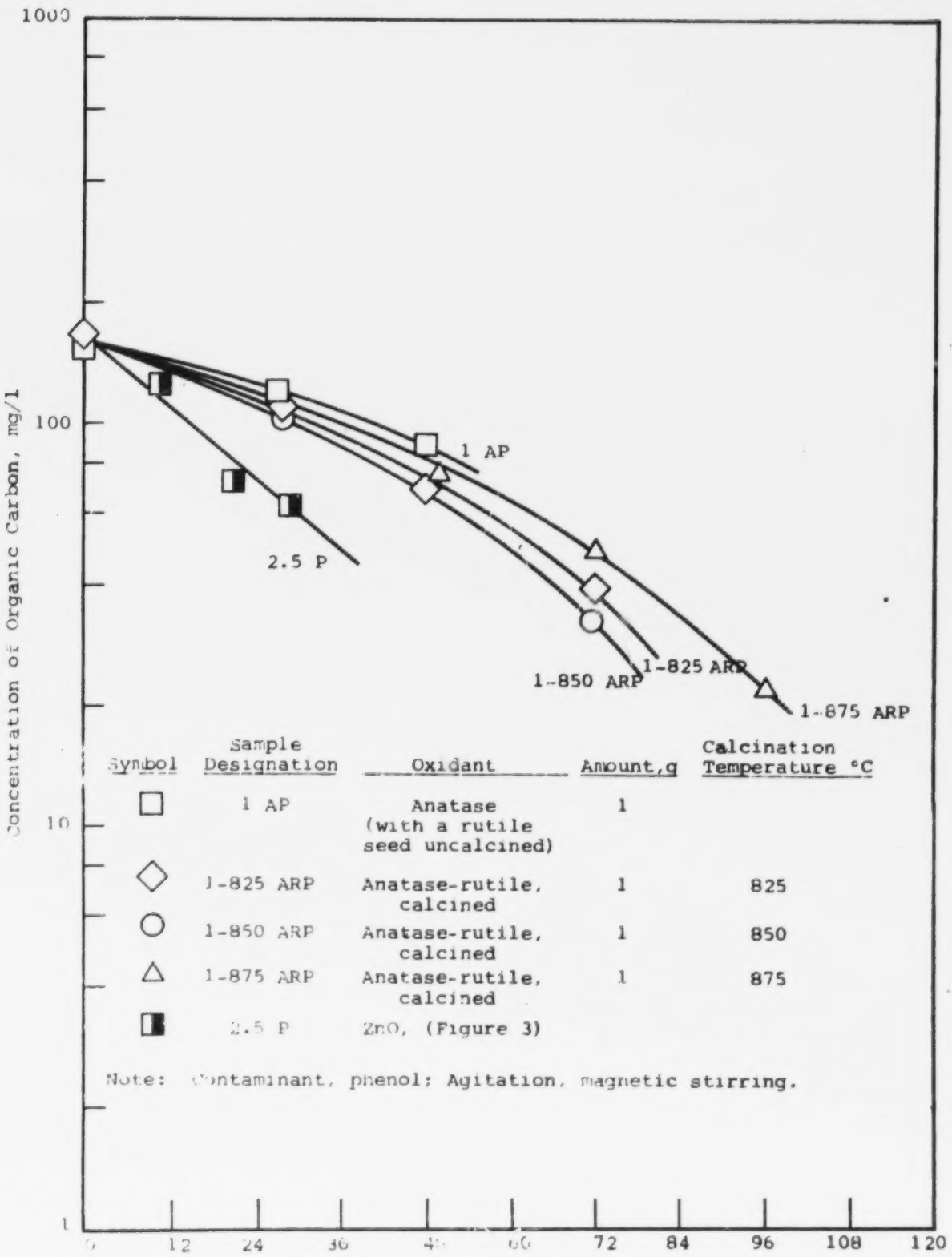


Figure 9

OXIDATION OF PHENOL WITH ANATASE AND ANATASE-RUTILE PREPARED BY CALCINATION AT DIFFERENT TEMPERATURES

Table 7
(Plotted in Figure 9)

OXIDATION OF PHENOL WITH ANATASE AND ANATASE-RUTILE PREPARED BY CALCINATION AT DIFFERENT TEMPERATURES

| Sample | Catalyst | Calcination Temperature °C | Time, hr | Concentration mg/l Organic Carbon | Concentration mg/l $H_2O_2$ | Time, hr | Concentration mg/l Organic Carbon | Concentration mg/l $H_2O_2$ | Time, hr | Concentration mg/l Organic Carbon | Concentration mg/l $H_2O_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-AP | Anatase | Not calcined | 0 | 155 | 0 | 25.7 | 120 | 0 | 48 | 89 | -- |
| 1-825 ARP | Anatase-Rutile | 825 | 0 | 166 | 0 | 26 | 110 | 3.3 | 48 | 70.0 | -- |
| 1-850 ARP | Anatase-Rutile | 850 | 0 | 168 | 0 | 26 | 105 | 3.5 | 48 | 67 | 3.0* |
| 1-875 ARP | Anatase-Rutile | 875 | 0 | 156 | 0 | 23 | 137 | 2.8 | 50 | 75 | -- |
| (cont.) | | | | | | | | | | | |
| 1-825 ARP | | | 72 | 39 | | | | | | | |
| 1-850 ARP | | | 72 | 32 | | | | | | | |
| 1-875 | | | 72 | 49 | | 96 | 24 | | | | |

*Oxidant, reported as $H_2O_2$

Note: All samples contained 1 g of pigment

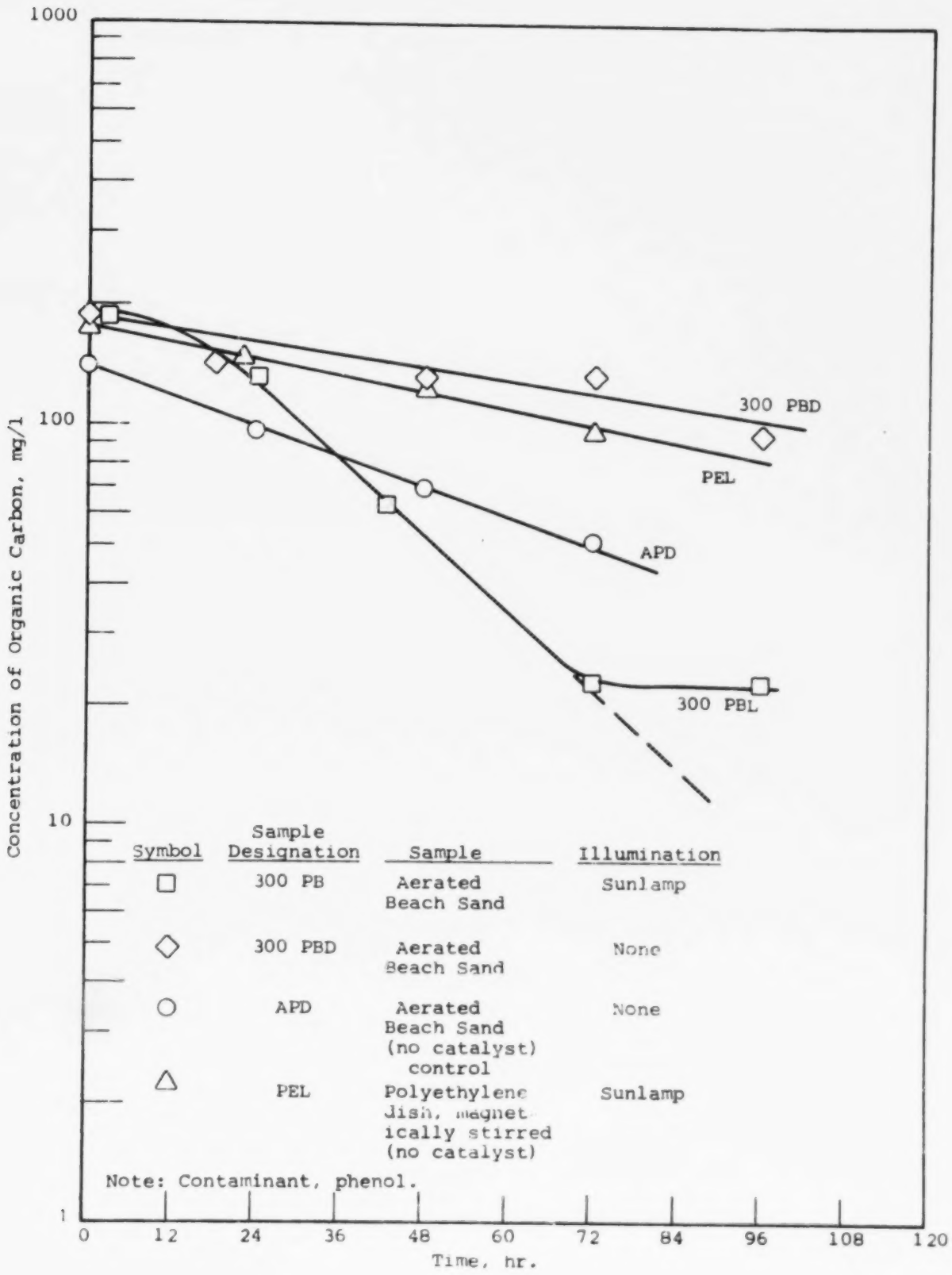


Figure 10

EFFECT OF ILLUMINATION ON OXIDATION OF PHENOL BY BEACH SAND

Table 8
(Plotted in Figure 10)

EFFECT OF ILLUMINATION ON OXIDATION OF PHENOL BY BEACH SAND

| Sample | Time, hr | Concentration mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration mg/l Organic Carbon | $H_2O_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 300 PBL | 0 | 172 | | 3.1 | 187 | | 24 | 132 | 13* |
| 300 PBD | 0 | 185 | 0 | 16 | 144 | | 48 | 131 | |
| PEL | 0 | 181 | | 22 | 149 | | 48 | 124 | |
| (cont.) | | | | | | | | | |
| 300 PBL | 42.5 | 54 | | 72 | 23 | 11* | 94 | 23 | |
| 300 PBD | 72 | 134 | | 96 | 96 | | | | |
| PEL | 72 | 96 | | | | | | | |

| Sample Designation | Sample | Illumination |
|---|---|---|
| 300 PBL | Aerated Beach Sand | Sunlamp |
| 300 PBD | Aerated Beach Sand | none |

| Sample Designation | Sample | Illumination |
|---|---|---|
| APD | Aerated Beach Sand (no catalyst) control | none |
| PEL | Polyethylene dish, magnetically stirred (no catalyst) | Sunlamp |

*Oxidant, reported as $H_2O_2$

to particulate organic matter. All samples were whole samples, i.e., they included any particulates generated by the agitation. Sample PEL shows that the oxidation is primarily photocatalytic and not simply due to photolysis.

The intensity of 3000-3800Å of sunlight is somewhat lower than that of the sunlamps so the natural process may be somewhat slower. On the other hand, in the range of about 3800-4200Å, sunlight is much stronger than the sunlamps, thus the oxidation rates of sunlamp vs. solar irradiation is a question of the relative effectiveness of radiation bands. Unfortunately time did not permit further exploration of this matter.

## OXIDATION OF PHENOL WITH THE ACE GLASS COMPANY PHOTOCHEMICAL APPARATUS

The photochemical apparatus consists of a medium-pressure mercury arc contained in a water-cooled quartz jacket which in turn is immersed in a Pyrex jacket. The sample to be irradiated is introduced into the annular space between the quartz and Pyrex containers, where it receives virtually all of the irradiation. Provision is made for sparging, and the exposure space may be pressurized.

The 450-watt mercury arc lamp provides about 0.063 watts/$cm^2$ of effective illumination vs. about 0.0032 watts/$cm^2$ for the sunlamps. The increase in oxidation rate due to the higher intensity was quite modest, as can be seen from comparing Figures 8 and 11. Figure 11 also represents an attempt at acceleration of oxidation by dye sensitization which is widely used to broaden the range of spectral absorption in electrophotography. Without a Pyrex filter (sample RB#1 [rose bengal])(Figure 11) the dye is bleached in a few minutes. We believe RB#2 (Figure 11) represents true dye sensitization but the dye oxidized too rapidly for dye sensitization to be of practical interest.

Sudan orange is much more oxidation-resistant than rose bengal but does not increase photosensitivity. The use of high

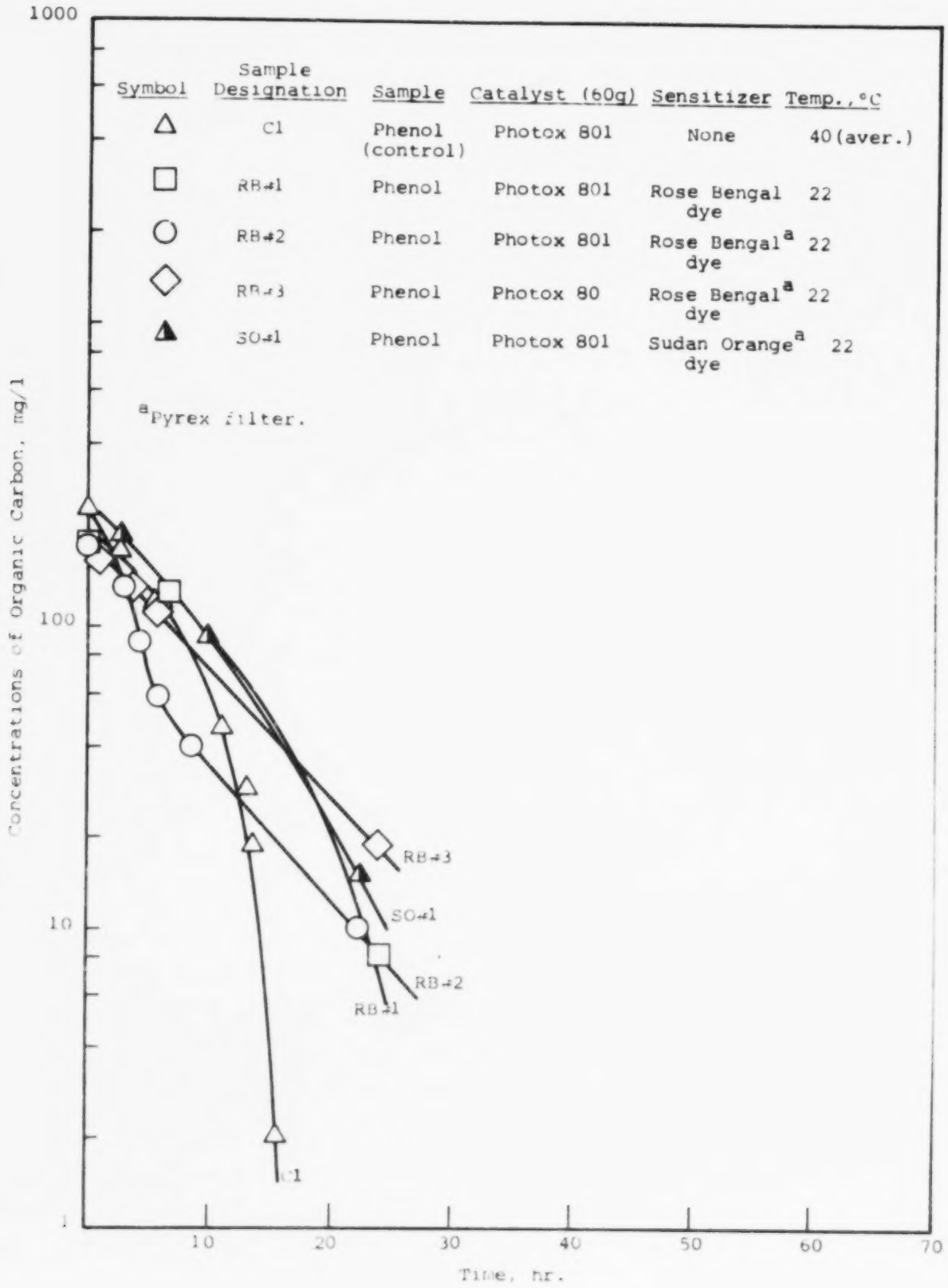


Figure 11

EFFECT OF DYE SENSITIZER ON PHOTOCATALYTIC OXIDATION IN PACE GLASS PHOTOCHEMICAL APPARATUS

Table 9
(Data plotted in Figure 11)

EFFECT OF DYE SENSITIZER ON PHOTOCATALYTIC OXIDATION
IN ACE GLASS PHOTOCHEMICAL APPARATUS

| Sample | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ | Time, hr | Concentration, mg/l Organic Carbon | $H_2O_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C1 | 0 | 213 | | 0.5 | 219 | | 1.0 | 195 | | 2.75 | 177 | | 6.5 | 122 | |
| RB#1 | 0 | 184 | | 0.25 | 180 | 25 | 3 | 130 | | 24 | 14 | 44 (8 centrifuged) | | | |
| RB#2 | 0 | 184 | | 0.5 | 184 | | 3 | 133 | 56 | 4.5 | 88 | 62 | 5.5 | 58 | 60 |
| RB#3 | 0 | 215 | | 0.16 | 189 | | 1.3 | 169 | 46 | 3.4 | 135 | 56 | 5.4 | 110 | |
| SO#1 | 0 | 248 | | 0.75 | 227 | | 2.6 | 201 | | 6.1 | 118 | | 9.75 | 93 | |
| (cont.) | | | | | | | | | | | | | | | |
| C1 | 11 | 46 | | 13.5 | 19 | | 16.5 | 2 | | | | | | | |
| RB#2 | 8.5 | 41 | 58 | 22.5 | 10 | | | | | | | | | | |
| RB#3 | 24 | 19 | | | | | | | | | | | | | |
| SO#1 | 22.5 | 15 | | | | | | | | | | | | | |

| Sample Designation | Sample | Catalyst (60g) | Sensitizer | Temp., °C |
|---|---|---|---|---|
| C1 | Phenol (control) | Photox 801 | None | 40 (Aver.) |
| RB#1 | Phenol | Photox 801 | Rose Bengal dye | 22 |
| RB#2 | Phenol | Photox 801 | Rose Bengal[a] dye | 22 |
| RB#3 | Phenol | Photox 80 | Rose Bengal[a] dye | 22 |
| SO#1 | Phenol | Photox 801 | Sudan Orange[a] dye | 22 |

loadings of ZnO (60 g/l) was an attempt to compensate for the short path exposed to the radiation, approximately ½ inch in the photochemical apparatus as compared to 1½ inch for the magnetically stirred samples. This may have been ill-advised since data at 10 and 20 g ZnO per liter showed somewhat faster oxidation rates. However, it was assumed that since 20 g/l was better than 10 g/l (not shown) still higher loadings would be better. The 10 g/l ZnO sample dropped to 10 mg/l organic carbon in 12 hours whereas the 20 g ZnO/l dropped to 10 mg/l organic carbon in 8 hours. Comparable time for 60 g/l ZnO loading from Figure 12, sample C1, 10 mg/l organic carbon was reached in 14 hours. All tests started at about 220 mg/l organic carbon. The temperature of the solution in these runs fluctuated from 30° to 50°C.

RB#3, on Figure 11, is a comparison of Photox 80, a zinc oxide reputed to be about twice as sensitive as Photox 801 in the visible when dye sensitized and is directly comparable to RB#2. It appears that this oxide is perhaps less effective than Photox 801 under these conditions. From this it is evident there is only a general relationship (if any) between the photoconductor properties of the pigment and its photocatalytic properties. Thus, Photox 801 may have been a poor choice. In view of the very large number of variables, it was imperative to standardize on one ZnO catalyst.

After brief raw sewage oxidation studies described subsequently, work with the Ace glass equipment was discontinued. It was only recently discovered that the catalyst had a tendency to adhere to the quartz envelope during the course of the oxidation. While this did not appear to block much light, the adsorption of phenol oxidation products caused a black tar to form in the early stages which retards the oxidation to an unknown degree.

The tar film was discovered when a test was halted in the early stages of oxidation. It is not known if this was a factor in the sewage oxidation studies.

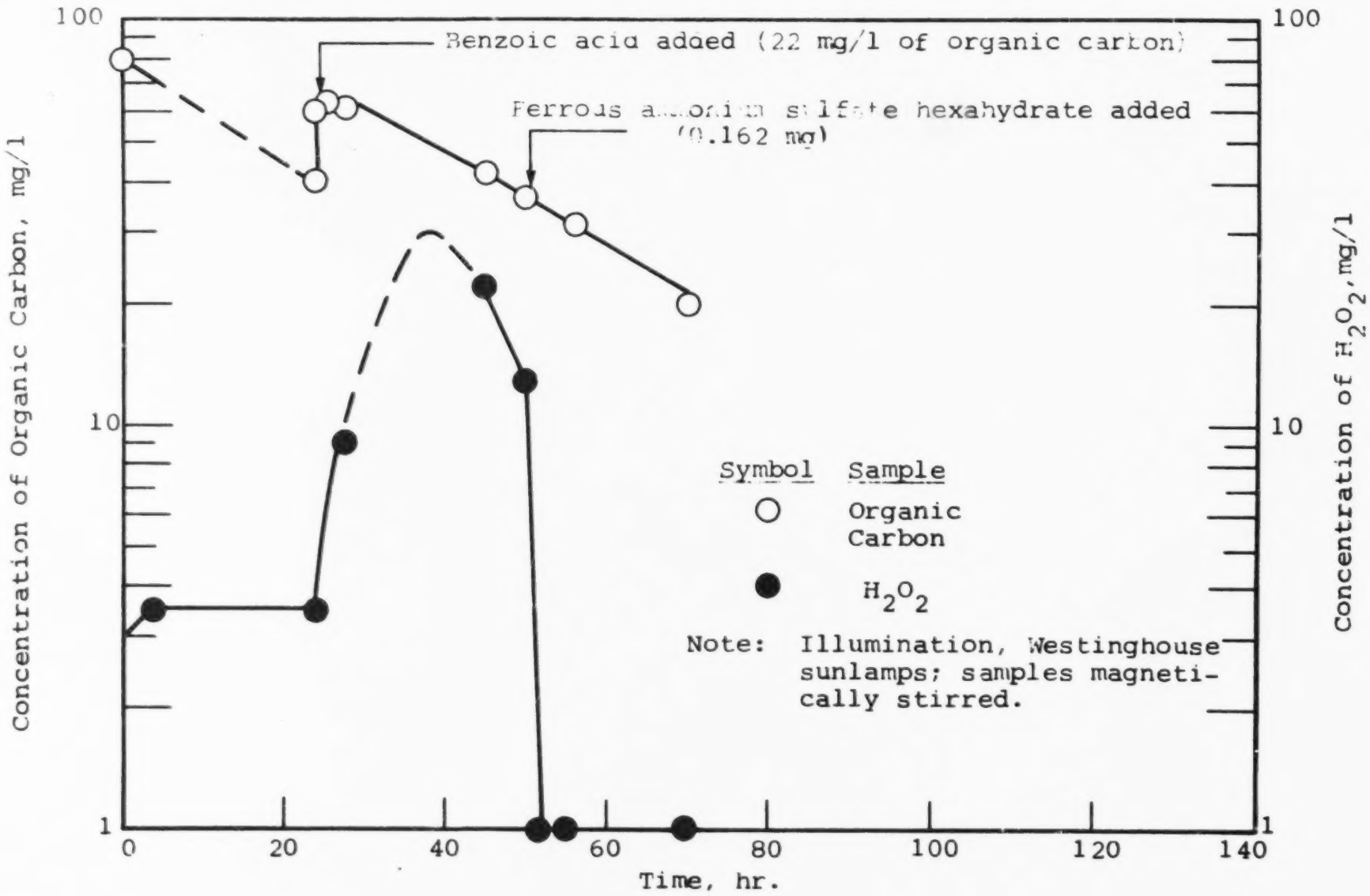


Figure 12

OXIDATION OF RAW SEWAGE

Table 10

OXIDATION OF RAW SEWAGE
(Mixed industrial and
domestic, Park Forest, Ill.)

| Time, hr | Concentration, mg/l | |
|---|---|---|
| | Organic Carbon | $H_2O_2$ |
| 0 | 80 | -- |
| After catalyst addition | 28[a] | -- |
| 24 | 28[a] | -- |
| 24 | 40 | 3.5 |
| After benzoic acid addition | 60 | -- |
| 28 | 63 | 9.0 |
| 27 | 60 | |
| 45 | 42 | 22 |
| 50[b] | 37 | 13 |
| 51 | -- | 0 |
| 56 | 31 | 0 |
| 70 | 20 | 0 |

[a]Values not reliable as explained in the text.

[b]Added $Fe^{2+}$ catalyst.

OXIDATION OF RAW SEWAGE

One experiment, (Figure 12), was conducted with mixed sanitary and industrial sewage magnetically stirred under sunlamps. Although our initial organic carbon oxidation data at 5 minutes and 1 hour are now known to be faulty, the experiment did represent an attempt at homogeneous catalysis. Bishop, et al.[9] have shown that ferric and ferrous ion catalyze $H_2O_2$ decomposition with formation of hydroxyl radicals, which, at about pH 4, oxidizes substantial amounts of organic carbon.

Chambron and Giraud[10] reported up to 98% catalytic oxidation of sodium lauryl sulfate by $H_2O_2$ with cupric, ferrous and manganous ion. However, they used $H_2O_2$ concentrations of approximately 3 wt %.

In our experiment, mixed industrial and domestic raw sewage was filtered through S & S 597 filter paper and the organic carbon was determined at the outset. This value started at 80 mg/l organic carbon and dropped almost immediately to 28 mg/l organic carbon. This rapid drop was subsequently proved to be a sampling error. This sewage contained varying amounts of "soluble" oil as evidenced by its typical opalescent appearance. In tests of known "soluble" oil concentration, ZnO breaks the emulsion and allows the oil to float on the surface. This fact is obscured by the zinc oxide; unless great care is taken to agitate the sample thoroughly, wide variations occur. In the case of the actual sewage, a fortuitous check value at 2 hours gave the reading undeserved credency, initially. For this reason, we have omitted data prior to the 22 hour point, which we believe to be valid, as well as subsequent measurements, since the oxidation follows the usual first order kinetics. The principal objective here was an attempt to produce hydroxyl radical by decomposing $H_2O_2$ with $Fe^{2+}$ catalyst after first enhancing $H_2O_2$ formation by the addition of benzoic acid. Although, as can be seen from Figure 12, the $H_2O_2$ dropped immediately to zero upon addition of the $Fe^{2+}$ catalyst, there was no effect on the organic removal rate.

Two samples of sewage (not shown) were run in the photochemical apparatus at 60 g/l zinc oxide. One sample consisted of mixed industrial and domestic sewage and the other was domestic sewage only. Due to heavy spring rains, we were unable to obtain samples with appreciable soluble organic matter as a result of rain-water dilution. The domestic sewage dropped from an initial 20 mg/l to 10 mg/l organic carbon in 7 hours; the mixed sewage dropped from an initial 33 mg/l to 20 mg/l in about 3 hours. Both samples leveled off, and further illumination for 3-4 hours had no effect. Both samples had been filtered through fiber glass filter paper. The residual organic may have been in colloidal form.

## BACTERICIDAL PROPERTIES OF IRRADIATED ZINC OXIDE SLURRIES

A final experiment was conducted to determine the bactericidal properties of illuminated zinc oxide. The test was conducted in saline solution with E. coli under the Westinghouse sunlamps in 2500 ml culture flasks in a low speed shaker. Although the zinc oxide showed a higher kill rate at 30 minutes and at 2 hours, the differences, compared with an illuminated control, were not considered statistically significant. The validity of the test was further diminished by the fact that oxidation of phenol in the same apparatus was substantially less than in crystallizing dishes with the same illumination and ZnO concentration and time of exposure. The reason for this is not clearly understood, since Pyrex transmits about 90% of the radiation in this region (3000-4000Å). It may be that the angle of incidence (variable from 0 to about 45° due to the contours of the flask) resulted in a much higher reflectance than if it had been normal to the light source. Zinc oxide of both 1 g/l and 10 g/l ZnO had no inhibitory effect on the growth of E. coli in the dark in nutrient.

While repeating the photo-oxidation tests with nutrient in open containers was considered desirable, expiration of time and funds did not permit this; thus, the question of the bactericidal

and/or bacteriostatic properties of illuminated photocatalysts is left in doubt.

## DISCUSSION

Although our original concept looked for the reaction of oxidant with organic materials, it is probable that the mechanism entails the direct reaction of an active oxygen species, atomic oxygen or singlet excited state molecular oxygen. From Figures 3, 4, and 7, it is evident that beyond a certain level of organic matter, the oxidant concentration has little relationship to organic level. In the case of zinc oxide, Markham and Laidler[5] attributed this result to the fact that organic molecules are adsorbed at the $H_2O_2$ decomposition sites, thus favoring the formation reaction and inhibiting the decomposition reaction. This apparently holds true for our oxidant as well (see Table 8). It must also be inferred that oxidant level is not a direct measure of catalyst effectiveness. Although zinc oxide apparently produces the highest oxidant level and apparently is the most effective oxidizer (Table 7), the actual oxidation data must be viewed with some reservation since they may represent merely differences in absorption of sunlamp irradiation of $TiO_2$ vs. ZnO. The actual surface area of the pigment is also an important factor.

We suggest that three conditions must be satisfied to achieve oxidation of an organic molecule.

(a) the molecule must be adsorbed at, or be in the vicinity of the active site on the catalyst.

(b) light energy of suitable wavelength (below about 4200Å) must impinge on the active site.

(c) dissolved oxygen must be present to replace the active oxygen species displaced by the radiation.

From these considerations, everything else being equal, the higher the concentration of contaminant the faster the rate of oxidation. Thus it would appear that photocatalytic oxidation will find its greatest utility in problems of industrial waste treatment where massive contamination is involved.

In our sunlamp exposures, we exceeded the manufacturer's recommended use period of 2000 hours by a factor of 2.5; however,

not until the end of this period did a noticeable decrease in oxidation rates appear. Extrapolation of the manufacturer's life-intensity curves, shows that the tubes dropped to perhaps 20% of their original value before a decrease in efficiency could be noted. From this, we infer that with this light source, the limiting parameter is the number of active sites on the catalyst surface and not the intensity of the source until it is greatly attenuated.

Despite a very large number of tests, we find ourselves without firm data on such a basic factor as the performance of various zinc oxides. The selection of Photox 801 on the basis of the $H_2O_2$ equilibrium was perhaps unfortunate; Photox 80 is a much better electrophotographic material, but as Figure 11 indicates, it is evidently not as good a photocatalyst.

Time did not permit a definitive investigation of temperature-dissolved oxygen relationships; however, we think the level of dissolved oxygen is not as important as the rate at which dissolved oxygen is replaced. Thus, vigorous agitation at elevated temperature would favor faster kinetics, despite lower dissolved oxygen level.

The premise upon which the investigation was undertaken has been amply confirmed. It is definitely possible to oxidize a number of known organic materials as well as a substantial portion of those in sewage by photocatalytic techniques. The evidence that this process occurs in nature is convincing and of great potential significance in pollution control.

## FUTURE WORK

Since it appears that with sunlamps, at least, the limiting factor is the number of reactive sites on the catalyst particle, examination of the wide variety of photocatalytic materials available would be fruitful. A brief investigation under the present program produced a substantial advance in $TiO_2$ performance. The anatase used contained a rutile seed crystal, which probably produces more crystallites in the anatase-rutile transition stage, with consequent greater photosensitivity. This result might further be enhanced by water quenching from the calcination temperature and/or by impurity doping.

An examination of the various grades of zinc oxide might reveal much more active types than the ones we used. The experiments with one type of beach sand suggest that a large number of catalysts are available in natural form which might be isolated and adapted to photocatalytic applications.

## INTERACTION OF IONIZING RADIATION WITH METAL OXIDE CATALYSTS

This approach is based on work of Yamamoto and Oster[6] who studied the polymerization of calcium acrylate and acrylamide in aqueous media under the influence of ionizing radiation. These investigators reported an "enormous" increase in polymerization effect when zinc oxide was added to the system. It appears reasonable that photo-oxidation would show a similar acceleration.

In such a system, a number of advantages over the photochemical system would accrue. Most importantly, the radiation would penetrate the slurry to a considerable depth so that much less surface area would need to be exposed. Higher efficiency should result because of the increased likelihood of the radiation striking an active site. Finally, the energy cost should be much lower and the time of exposure much shorter.

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APPENDIX

# Analytical Procedures for the Determination of Low Concentrations of Hydrogen Peroxide in Aqueous Solutions

## I. INTRODUCTION

The following outlines in detail the step-by-step procedures to be followed in analyzing for hydrogen peroxide by the potassium iodide method. None of the theoretical aspects will be included in this description; however, the precautions to be observed and special techniques to be followed will be described in each step.

## II. EQUIPMENT

- 1 - 5 ml micro burette 1/100 ml graduations
- 2 - 1 ml pipette
- 1 - 2 ml pipette
- 1 - 10 ml pipette
- 2 - 10 ml graduate
- 1 - 25 ml graduate
- 4 - 150 ml Erlenmeyer Flasks
- 2 - glass stirring rods
- 1 - wash bottle distilled water
- 2 - 1 qt stoppered bottle
- 1 - 1 pt stoppered bottle
- Eye droppers
- 1 - acid dropping bottle
- 1 - trip balance
- 1 - stop watch

Bausch and Lomb Spectrophotometer "Spectronic 20" with constant voltage transformer.

## III. CHEMICAL REAGENTS

1. Distilled water
2. 0.01 N standardized sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$). Supplies of this solution may be obtained from chemical supply houses. It should be kept in ordinary stoppered bottles to avoid contamination or concentration changes. (Dilute 0.1 N standardized solution to 0.01 N).
3. Use $H_2SO_4$ acid in KI to maintain acid pH.
4. 1 N potassium iodide solution: The potassium iodide (KI) solution should be prepared daily by adding sufficient distilled water to approximately 150 g of reagent grade KI to make up 900 ml of solution. This solution must

be stored in an amber bottle and cannot be used if over 24 hours old.

5. Indicator: Starch indicator is prepared daily by adding 5 g of reagent grade soluble starch to 100 ml of boiling distilled water and stirring vigorously. The solution must be clear upon cooling. The indicator is useable only on the day prepared.

Sampling Procedure

We assume a 10 ml sample is representative of the solution we want to determine.

In a 20 ml beaker we place 10 ml of our unknown. Add 5 drops of 0.5 N $H_2SO_4$ - 20 drops of KI (in solution) - 5 drops of starch solution.

The stop watch is started as the KI is added.

Pipette 1 ml of sample, add to 10 ml graduate, dilute to 10 ml -- label "A".

Pipette 1 ml of sample, add to 25 ml graduate, dilute to 20 ml -- label "B".

Pipette 2 ml of sample, add to 10 ml graduate, dilute to 10 ml -- label "C".

After diluting, shake to evenly distribute solution.

Take B graduate, rinse the B & L test tube and fill to mark. Use spectronic 20 - record transmission.

Take A graduate, rinse the B & L test tube back and forth, fill to mark - record transmission.

Take C graduate, rinse the B & L test tube back and forth, fill to mark - record transmission.

The dilutions and reading should be all done in a 5 minute period. Total time on stopwatch should be under 10 minutes.

The transmission values are then used on Figure A-1 to determine the concentration of unknown solution.

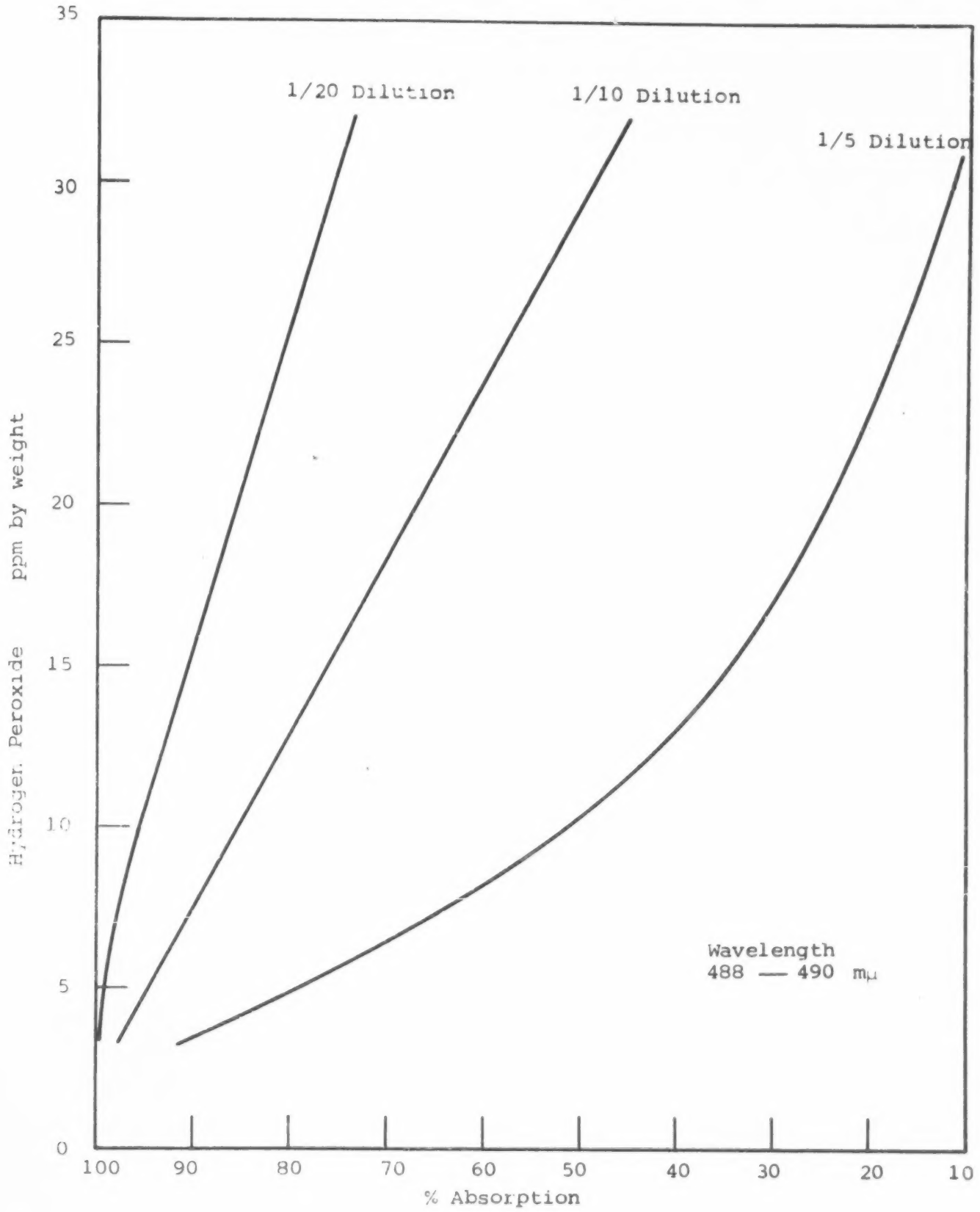


Figure A-1

ABSORPTION OF STARCH IODIDE
AT VARIOUS CONCENTRATIONS

Table A-1

ABSORPTION OF STARCH IODIDE AT VARIOUS CONCENTRATIONS

| Sample No. | Dilution Value | Titration Value | 1/5 Dilution | 1/10 Dilution | 1/20 Dilution |
|---|---|---|---|---|---|
| | | | Absorption Values | | |
| A | 3.29 ppm | 4.25<br>3.4* | 92 | 97 | 99-100 |
| B | 6.58 | 7.47<br>6.62* | 71 | 93 | 98 |
| C | 9.87 | 10.07<br>9.85* | 54 | 86 | 96 |
| D | 13.16 | 13.2<br>12.4* | 43 | 81 | 93 |
| E | 16.45 | 16.3<br>15.4* | 34 | 75.5 | 91 |
| F | 19.74 | 19.9<br>19.0* | 29.5 | 70.5 | 87 |
| G | 23.03 | 22.8<br>21.9* | 19 | 61.0 | 83.5 |
| H | 26.32 | 25.8<br>25.0* | 18 | 59.0 | 81 |
| I | 29.61 | 28.6<br>27.7* | 14 | 54.0 | 82 |
| J | 32.90 | 32.4<br>31.6* | 11 | 47.0 | 73 |

*Corrected for distilled water blank.
Dilution was made with distilled water.

10 ml tap water $\simeq$ 3 drop (0.14 ml Thiosulfate solution)
10 ml distilled water $\simeq$ 1 drop (0.05 ml Thiosulfate solution).

Titration Procedure can be used as a check.

Titrant 0.01 N Sodium Thiosulfate

20 ml of 1 N Potassium Iodide (KI)
20 drops of 0.5 N $H_2SO_4$
10 ml of sample solution  Start stopwatch
5 ml of starch solution

Start titrating after 5 minutes of reactive digestion.

When solution starts going from purple → brown, add the thiosulfate dropwise at a very slow rate until a sharp color change from purple brown to water white is obtained. Wait 5 seconds between drops at this stage to avoid going past the end point.

Amount of thiosulfate used is recorded.

Equations:

$$H_2O_2 + 2KI \longrightarrow I_2 + 2KOH$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Equivalent:

1 mole $H_2O_2$ — 1 mole $I_2$ — 2 moles $Na_2S_2O_3$

17 grams $H_2O_2$ — 1 mole $Na_2S_2O_3$ (1 liter of 1 normal solution)

1 cc of 0.01 N $Na_2S_2O_3 = \frac{17 \times 0.01}{1000} = 0.00017$ grams $H_2O_2$

END